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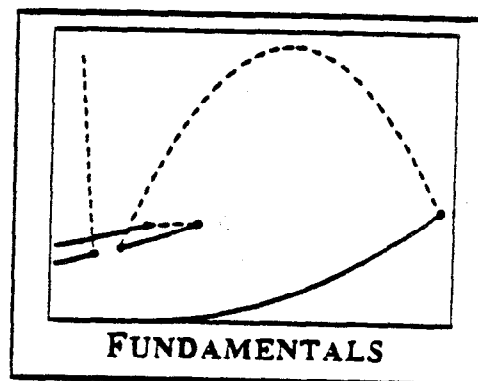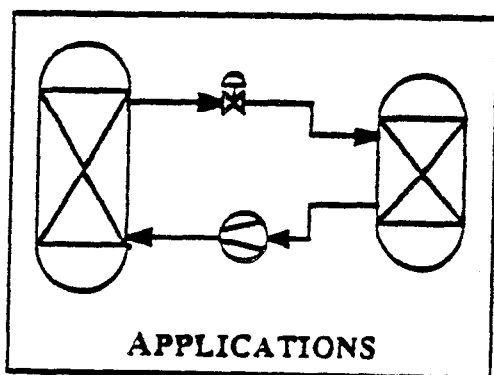
BOSTON, MASSACHUSETTS
LONG WHARF MARRIOTT HOTEL
20 – 22 MAY 1991

EXTRACTION DYNAMICS AND OPTIMIZATION FOR THE SUPERCRITICAL FLUID EXTRACTION OF EVENING PRIMROSE OIL.

by
Fabio Favati[1], Jerry W. King[2]
and Monica Mazzanti[2]

[1] Istituto di Industrie Agrarie
dell'Universita,
Via S. Michele, 4 - 56123 Pisa, Italy.
[2] Food Physical Chemistry Research
National Center for Agricultural
Utilization Research - USDA/ARS
1815 N. University Street - Peoria, IL 61604.

ABSTRACT

Evening primrose oil (EPO) is a natural source of gamma-linolenic acid (GLA), an agent of potential therapeutic value in the treatment of several diseases. Previous studies have reported the application of supercritical fluid extraction (SFE) for the removal of this valuable oil from the seed matrix, however limited information exists as to the optimal conditions required for the SFE.

In this paper the extraction of EPO with supercritical CO_2 (SC-CO_2) was studied over the pressure and temperature range of 20-70 MPa and 40-60°C, respectively. The analysis of the collected data permitted the calculation of the EPO solubilities in the SC-CO_2, which ranged from 0.21 g oil/100 g CO_2 at 20 MPa and 60°C, to 4.78 g oil/100 g CO_2 at 70 MPa and 60°C.

Further characterization of the extraction kinetics included a study of the SFE efficiency as a function of the fluid flow rate. Varying the CO_2 flow rate over the range 9-27 g/min, did not cause appreciable differences in the EPO solubilities and recoveries.

INTRODUCTION

In human metabolism gamma-linolenic acid (18:3 n-6) is an important intermediate metabolite for the synthesis of precursors to prostanoids (1). However, several factors, including stress, ageing, diabetes, or consumption of alcohol can reduce or inhibit the production of GLA, leading to a variety of ailments. Consequently, the possibility of restoring adequate levels of GLA through dietary supplementation has raised interest in oils rich in GLA, such as the oil contained in the seed of the evening primrose (Oenothera biennis L.) (2-5).

The evening primrose oil (EPO) contains a significant amount of GLA (8-12% by weight) (6), and commands a high retail market price, approximately US$ 480.00 per kg of oil. EPO is conventionally obtained by either mechanical expression of the seeds or solvent extraction by hexane. However, in order to avoid any undesirable physicochemical changes of GLA these procedures must be conducted under moderate conditions, e.g. mild temperatures.

The use of supercritical carbon dioxide (SC-CO_2) for the extraction of lipid moieties is well documented in the literature (7-13), and the low critical temperature of CO_2 (31°C) allows the extraction of heat-labile compounds at relatively low temperatures, therefore reducing the possibility of degradation. Consequently, supercritical fluid extraction (SFE) with CO_2 as the solvent could represent a viable alternative technology for the removal of the oil from the evening primrose seeds. An additional benefit of using SC-CO_2 is the easy separation of the solvent from the extract, thereby leaving no organic solvent residues in the EPO.

The objective of this study was to acquire data on EPO solubility in SC-CO_2, the rate of the extraction, and the influence of the process parameters on the mass transfer rate. Such data are required for the optimization and design of an efficient SC-CO_2 extraction process.

MATERIALS AND METHODS

The evening primrose seeds, harvested in England in 1988, were kindly provided by Efamol Ltd (Guilford, England). Their oil content was 26.1% by weight (b.w.) on a dry basis. GLA content was determined by GLC and represented 10% b.w. of the total fatty acids.

The experiments were performed with the apparatus shown in Figure 1 and described in detail elsewhere (14). The extraction vessel consisted of a 316 SS tube, pressure rated to 76 MPa at room temperature, with dimensions of 1.75 cm i.d. x 30 cm. The tests were conducted on samples of approximately 50 g, and the seeds were ground to pass a 0.355 mm sieve immediately before being loaded into the extraction vessel. Moisture and oil content of the seeds were determined according to standard AOCS methods (15).
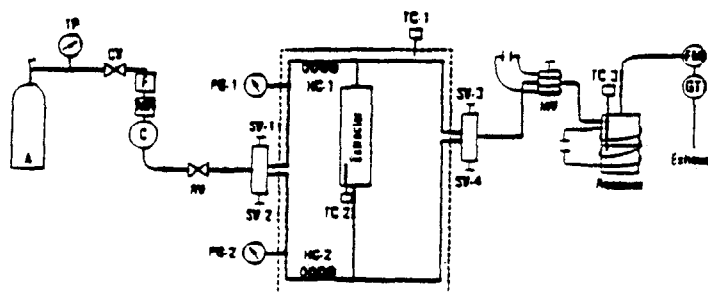

Fig. 1 - Supercritical fluid extraction system. Dashed lines indicate thermostated region. (A= CO_2 cylinder; TP= tank pressure gauge; CV= check valve; F= particulate filter; MF= mass flow meter; C= air-driven gas booster compressor; RV= relief valve; SV-1, 2, 3, 4= valves; PG-1,2= pressure gauges; HC-1,2= thermal equilibrating coils; TC-1,2, 3= thermocouples; MV= micrometering valve; FM= flow meter; GT= gas totalizer).

The extractions were carried out at 20, 30, 50 and 70 MPa, over the temperature range of 40-60°C. A standard amount of CO_2 (2.5 kg) was used in each experiment, and the extracted material was collected at discrete intervals, after 125, 250, 375, 500, 750, 1,000, 1,500 and 2,500 g of CO_2 passed through the seed bed. Different CO_2 mass flow rates (9, 18 and 27 g/min) were utilized in this study. The CO_2

mass flow rate was assessed by using a mass flow meter (Model D6, Micro Motion Co. Boulder, CO) placed before the compressor, as well as by converting to grams the volume of CO_2 recorded by a gas totalizer (Singer Model DTM-115 American Meter Division, Philadelphia, PA) connected to the receiver.

A small quantity of water was co-extracted with the oil, therefore the extracts were diluted in anhydrous diethyl ether and dried over anhydrous sodium sulfate. The extraction yields were then determined gravimetrically after removing the solvent at room temperature and reduced pressure.

RESULTS AND DISCUSSION

In the SFE of oil bearing materials the mass transfer kinetic of the process is strongly dependent on the particle size of the extracted substrate. Studies conducted on soybean seeds and rapeseeds have shown that the efficiency of the extractions could be improved when the seeds were flaked or ground (10,16-19). Due to the very tiny dimension of the evening primrose seeds, about 1 mm in length, it was not possible to flake the seeds. Therefore in order to increase the surface area of the material in contact with the stream of CO_2 the seeds were finely comminuted in a grinder.
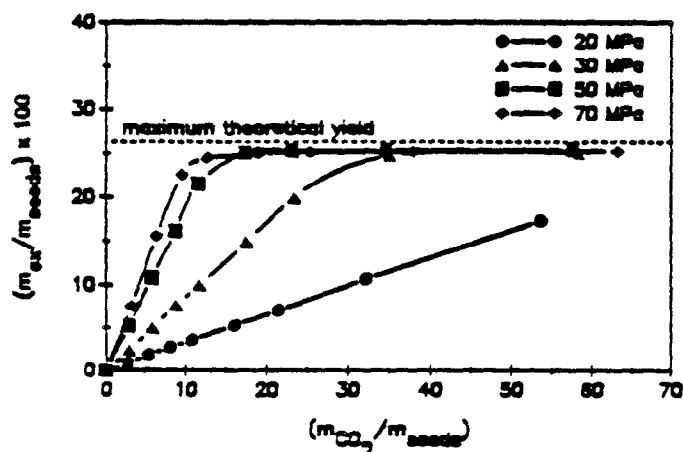

Fig. 2 - Evening primrose oil extraction yields at 40°C and different pressures as a function of the specific mass of CO_2 passed through the extraction vessel.

The extractions were initially conducted with a CO_2 mass flow rate of 18 g/min, and the collected experimental data permitted the calculation of the EPO solubility in SC-CO_2 over the range of pressure and temperature tested. Typical extraction curves are shown in Figure 2, where the extraction yields for the tests conducted at 40°C were plotted versus the specific solvent mass. The initial linear portion of the curves indicated a constant rate of extraction over an extended period of time. This indicated that the extraction was governed by the equilibrium solubility of the oil in the extraction fluid. Similar plots were also obtained for the tests conducted at 50 and 60°C, and the slope of the linear portion of the curves was assumed to represent the EPO solubility in SC-CO_2 at the given experimen-

tal conditions (20).

The calculated EPO solubility values are plotted in Figure 3 as a function of the extraction conditions. It can be observed that above the pressure of 30 MPa, an increase in the extraction temperature had a positive effect on the oil solubility, whereas under 30 MPa the effect was reversed. This inversion in the solubility behavior of lipid moieties in SC-CO_2 has been also reported for the SFE of oil from soybeans, canola and jojoba seeds (8, 16, 21, 22). The above trend can be explained by taking into account the effect of the extraction temperature on both the solvent and the solute; i.e., the vapor pressure of the oil is increased, while the density of the CO_2 is reduced. However, below a specific pressure a decrease in solute solubility is observed due to the decrease in the CO_2 density.
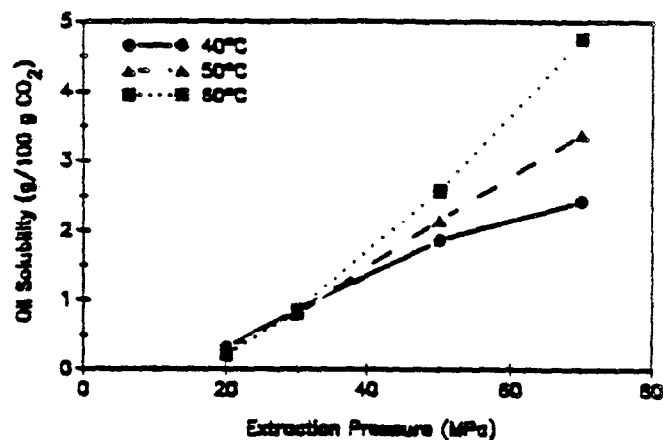

Fig. 3 - Evening primrose oil solubility in SC-CO_2 as a function of the extraction pressure at different temperatures.

With the objective of isolating the effect of the extraction temperature on the vapor pressure of the solute (oil) from that on the density of the solvent (SC-CO_2), some of the calculated EPO solubility values were plotted as a function of the extraction temperature and SC-CO_2 density. In Figure 4 the lines connect points representing the EPO solubility in SC-CO_2 as determined in the described experiments conducted at different extraction conditions (pressure and temperature), but at similar solvent densities. The data show that at constant CO_2 density, raising the extraction temperature always caused an increase of the amount of oil dissolved in the supercritical fluid. However, increasing the temperature from 40 to 60°C, resulted in the greatest enhancement in EPO solubility when operating the extractor at the highest CO_2 density.

With the apparatus utilized in this study, the CO_2 leaving the receiver was vented, but in an industrial scale process, it would be much more appropriate to recirculate the extraction fluid. On the basis of the above solubility data, the best operating conditions for the extraction of the EPO would be 70 MPa and 60°C, and the recovery of the oil could be accomplished in a separation vessel maintained at a lower pressure. A good separation of the oil phase from the solute-laden stream of CO_2, could be achieved operating at 20 MPa and 60°C,

when the EPO solubility in SC-CO_2 is twenty times less than at 70 MPa.
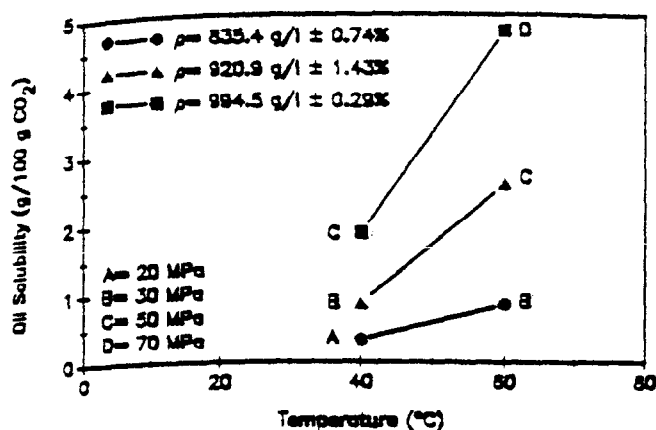

Fig. 4 – Influence of the temperature on evening primrose oil solubility in SC-CO_2 at constant solvent density.

Another fundamental parameter required for the optimization of the SFE process, is the flow rate of the extraction fluid. While it is important to provide a high CO_2 flow rate to ensure rapid depletion of the oil from the proteinaceous substrate, the residence time of the fluid in the extractor vessel should be long enough to ensure adequate mass transfer of the oil in the stream of SC-CO_2. The extraction yields obtained in experiments conducted at three different CO_2 flow rates (9, 18 and 27 g/min) are shown in Figure 5.
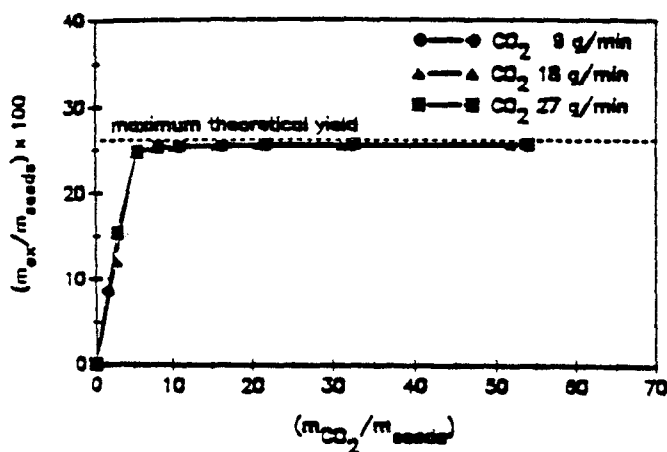

Fig. 5 – Evening primrose oil extraction yields obtained at 70 MPa and 60°C using different CO_2 mass flow rates.

In this case the system was operated at 60°C and at the pressure of 70 MPa. The plot shows no appreciable differences in the EPO extraction rates and the calculated oil solubilities were 4.86, 4.76 and 4.83 g oil/100 g CO_2 respectively for flow rates of 9, 18 and 27 g/min of CO_2. The experiments were repeated maintaining the extraction vessel at the pressure of 20 MPa and at the temperature of 40°C. In this case, the EPO extraction

yields did not change significantly when the CO_2 flow rate was varied over the range 9-27 g/min [(m_{ex}/m_{seeds})x100= 16.89 ± 2.7].
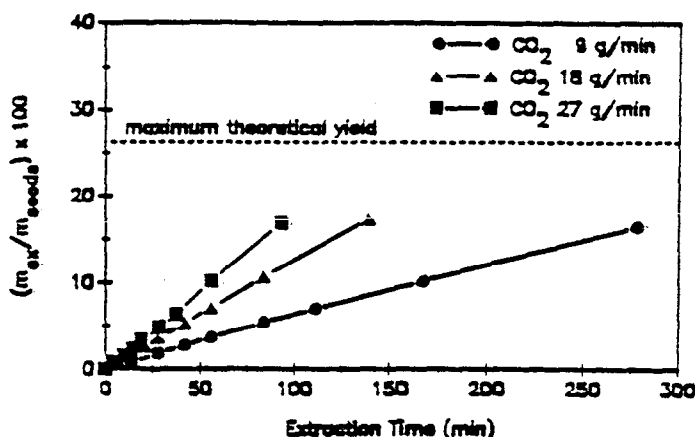

Fig. 6 – Evening primrose oil extraction yields as a function of the extraction time for experiments conducted at 20 MPa, 40°C and different CO_2 mass flow rates.

These results indicate that under the tested conditions the EPO removal was a sole function of the mass of extraction gas passed through the seed bed. However, with a higher flow rate a much more rapid extraction of the oil could be effected, resulting in a substantial reduction of the time required to deplete the seed matrix of the oil. The utilization of high solvent flow rate is very important especially when the SFE process is conducted at pressure and temperature conditions that result in a limited solubility of the oil in the supercritical solvent. This conclusion is supported by the results shown in Figure 6, were the extraction yields for the tests conducted at 20 MPa, 40°C and different CO_2 flow rates, are plotted as a function of the extraction time. The recovery of 65% of the available oil was achieved in less than 100 min when the CO_2 flow rate was maintained at 27 g/min, while nearly 300 min were necessary to obtain a similar EPO recovery when the flow of the solvent was set at 9 g/min.

In summary, the data collected in this study should be useful in the design and optimization of a SFE process for the recovery of EPO. The highest oil solubility was obtained operating the system at 70 MPa and 60°C. Changing the SC-CO_2 flow rate over the range 9-27 g/min. did not cause appreciable differences in the EPO recovery. This suggests that, in order to minimize the extraction time, the flow of the supercritical fluid should be set at the highest value.

DISCLAIMER

The mention of firm names or trade products

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